PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 :
A62D 1/08, A62C 13/00, 35/00

A1

(11) International Publication Number: WO 95/26218

(43) International Publication Date: 5 October 1995 (05.10.95)

(21) International Application Number: PCT/US95/03490

(22) International Filing Date: 21 March 1995 (21.03.95)

(30) Priority Data:
08/218,347 28 March 1994 (28.03.94) US

(71) Applicant: GREAT LAKES CHEMICAL CORPORATION [US/US]; P.O. Box 2200, Highway 52 N.W., West Lafayette, IN 47906 (US).

(72) Inventors: ROBIN, Mark, L.; 5411 Hillside Lane, West Lafayette, IN 47906 (US). IIKUBO, Yuichi; 2825 Barlow Street, West Lafayette, IN 47906 (US). SWEVAL, Mark, A.; 1226 Old Mill Lane, Lafayette, IN 47905 (US).

(74) Agents: HENRY, Thomas, Q. et al.; Woodard, Emhardt, Naughton, Moriarty & McNett, Bank One Center/Tower, Suite 3700, 111 Monument Circle, Indianapolis, IN 46204 (US).

(81) Designated States: AM, AU, BB, BG, BR, BY, CA, CN, CZ, EE, FI, GE, HU, JP, KG, KP, KR, KZ, LK, LR, LT, LV, MD, MG, MN, MX, NO, NZ, PL, RO, RU, SG, SI, SK, TJ, TT, UA, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ, UG).

Published
With international search report.

(54) Title: OZONE FRIENDLY FIRE EXTINGUISHING METHODS AND COMPOSITIONS

(57) Abstract

Methods of extinguishing a fire with compositions which include a hydrofluorocarbon and an acid-scavenging additive. The fire extinguishing compositions preferably include one or more hydrocarbons of the formula $C_xH_yF_z$, where $(y + z) = (2x + 2)$, and wherein y is less than or equal to x. The acid scavenging additive is preferably selected from the group consisting of terpenes, unsaturated oils, sodium bicarbonate, potassium bicarbonate, monoammonium phosphate, alkali metal halides and urea.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgystan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo			SE	Sweden
CH	Switzerland	KR	Republic of Korea	SI	Slovenia
CI	Côte d'Ivoire	KZ	Kazakhstan	SK	Slovakia
CM	Cameroon	LI	Liechtenstein	SN	Senegal
CN	China	LK	Sri Lanka	TD	Chad
CS	Czechoslovakia	LU	Luxembourg	TG	Togo
CZ	Czech Republic	LV	Latvia	TJ	Tajikistan
DE	Germany	MC	Monaco	TT	Trinidad and Tobago
DK	Denmark	MD	Republic of Moldova	UA	Ukraine
ES	Spain	MG	Madagascar	US	United States of America
FI	Finland	ML	Mali	UZ	Uzbekistan
FR	France	MN	Mongolia	VN	Viet Nam
GA	Gabon				

OZONE FRIENDLY FIRE EXTINGUISHING METHODS AND COMPOSITIONS

BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION

The present invention relates to the field of fire extinguishing compositions and methods, and particularly to compositions and methods employing compositions comprised of hydrofluorocarbons and acid scavenging additives.

DESCRIPTION OF THE PRIOR ART

The use of certain bromine-containing chemical agents for the extinguishment of fires is common. These agents are in general thought to be effective due to their interference with the normal chain reactions responsible for flame propagation. The most widely accepted mechanism for flame suppression is the radical trap mechanism proposed by Fryburg in Review of Literature Pertinent to Fire Extinguishing Agents and to Basic Mechanisms Involved in Their Action, NACA-TN 2102 (1950). It is generally accepted that compounds containing bromine act by interfering with free radical or ionic species in the flame; the presence of fluorine has not been considered as contributing to the fire extinguishing properties of a compound, but will impart stability, reduce toxicity and boiling point, and increase thermal stability.

Various halogenated hydrocarbons have been employed as fire extinguishants. Prior to 1945, three halogenated

extinguishing agents widely used were carbon tetrachloride, methyl bromide and bromochloromethane. For toxicological reasons, however, the use of these agents has been discontinued. The three fire extinguishing agents presently in common use are bromine-containing compounds, Halon 1301 (CF_3Br), Halon 1211 (CF_2BrCl) and Halon 2402 ($BrCF_2CF_2Br$). The effectiveness of these three volatile bromine-containing compounds in extinguishing fires has been described in United States Patent No. 4,014,799, issued to Owens. The National Fire Protection Association (NFPA) publication, the Fire Protection Handbook, Section 18, Chapter 2, entitled "Halogenated Agents and Systems" (1985) describes these agents in more detail.

Although the above named bromine-containing compounds are effective fire fighting agents, those agents containing bromine or chlorine are asserted to be capable of the destruction of the earth's protective ozone layer. For example, Halon 1301 has an Ozone Depletion Potential (ODP) rating of 10, and Halon 1211 has an ODP of 3. As a result of concerns over ozone depletion, the production and sale of these agents after January 1, 1994 is prohibited under international and United States policy.

The use of hydrofluorocarbons as extinguishing agents has been proposed only recently, for example as described in U.S. Patent 5,124,053 to Iikubo and Robin. Since the hydrofluorocarbons do not contain bromine or chlorine, the compounds have no effect on the stratospheric ozone layer and their ODP is zero. It has been discovered that certain of these compounds, especially those with a higher ratio of hydrogen to fluorine in the molecule, can decompose to some extent in a fire, producing hydrogen fluoride, HF, which is potentially damaging to personnel and equipment if formed in large quantities.

It is therefore an object of this invention to provide a method for extinguishing fires as rapidly and effectively as

the techniques employing presently employed fire extinguishing agents while avoiding the above-named drawbacks.

It is a further object of this invention to provide an agent for use in a method of the character described that is efficient, economical and environmentally safe with regard to ozone depletion.

SUMMARY OF THE INVENTION

Briefly describing one aspect of the present invention there is provided a method of extinguishing a fire that comprises introducing to the fire a fire extinguishing concentration of an extinguishant composition comprising, and preferably consisting essentially of, a hydrofluorocarbon and an acid-scavenging additive, and maintaining the concentration of the composition until the fire is extinguished. Fire extinguishing compositions comprising, or consisting essentially of, a hydrofluorocarbon and an acid-scavenging additive are also provided.

It is an object of the present invention to provide an effective method for extinguishing fires. Another object of the present invention is to provide a fire extinguishing method which utilizes particular combinations of hydrofluorocarbons and acid-scavenging additives which are effective at non-toxic levels.

It is a further object of the present invention to provide a fire extinguishing method which employs compounds that are environmentally safe, having low ozone depletion potential and greenhouse warming effect.

A further object of the present invention is to provide fire extinguishing compositions comprising blends of hydrofluorocarbons and acid-scavenging additives, which blends are effective and safe in use.

A further object of the present invention is to provide fire extinguishing compositions which produce reduced amounts of decomposition products compared to other fire extinguishing agents when employed in the extinguishment of fires.

Further objects of the present invention will be apparent from the description which follows.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

For the purpose of promoting an understanding of the principles of the invention, reference will now be made to preferred embodiments of the invention and specific language will be used to describe the same. It will nevertheless be understood that no limitation of the scope of the invention is thereby intended, such alterations, further modifications and applications of the principles of the invention as described herein being contemplated as would normally occur to one skilled in the art to which the invention relates.

In accordance with the present invention, it has been found that compositions comprising a hydrofluorocarbon in combination with an acid-scavenging additive provide particularly effective fire extinguishants at concentrations safe for use. Because the compositions contain no bromine or chlorine, they have an ozone depletion potential of zero. In addition, the compositions produce less decomposition products than the hydrofluorocarbon analogs, and hence are of reduced toxicity with regard to use in a fire scenario. In a related aspect, the invention relates to methods for extinguishing fires which are improved by using these compositions as the fire extinguishing agents.

The invention is directed to a non-toxic fire extinguishant comprising in combination:

(a) a hydrofluorocarbon of the formula $C_xH_yF_z$, wherein $(y+z) = (2x + 2)$, and wherein $y \leq x$; and

(b) one or more substances selected from the group consisting of terpenes, unsaturated oils, sodium bicarbonate, potassium bicarbonate, monoammonium phosphate, alkali metal halides and urea. The extinguishant compositions may preferably consist essentially of the hydrofluorocarbon and the acid-scavenger(s).

Specific hydrofluorocarbons useful in accordance with the present invention include trifluoromethane (CF_3H), pentafluoroethane (CF_3CF_2H), 1,1,1,2-tetrafluoroethane (CF_3CH_2F), 1,1,1,2,3,3-hexafluoropropane (CF_3CHFCF_2H), 1,1,1,3,3,3-hexafluoropropane ($CF_3CH_2CF_3$), 1,1,2,2,3,3-hexafluoropropane ($HCF_2CF_2CF_2H$), 1,1,1,2,3,3,3-heptafluoropropane (CF_3CHFCF_3), 1,1,1,2,2,3,3-heptafluoropropane ($CF_3CF_2CF_2H$), 1,1,1,2,2,3,3,4,4-nonafluorobutane ($CF_3CF_2CF_2CF_2H$), 1,1,1,2,3,4,4,4-octafluorobutane ($CF_3CHFCHFCF_3$) and 1,1,1,3,3,3-hexafluorobutane ($CF_3CH_2CH_2CF_3$). Other hydrofluorocarbons within the present invention are $C_3H_3F_5$, $C_4H_3F_7$, $C_5HF_3F_{11}$, $C_5H_2F_{10}$, $C_5H_3F_9$, $C_5H_4F_8$, and $C_5H_5F_7$.

Specific terpenes useful in accordance with the present invention include citral, citronellal, limonene, dipentene, menthol, alpha-pinene, beta-pinene, camphor, vitamin A beta-carotene, and isopropenyl-1-methylcyclohexene. The terpenes preferably comprise from about 0.1% to about 10% by weight of the extinguishing composition.

Specific unsaturated oils useful in accordance with the present invention include oleic acid, linoleic acid, palmitoleic acid and vaccenic acid. The unsaturated oils preferably comprise from about 0.1% to about 10% by weight of the extinguishing composition.

Specific alkali metal halides useful in accordance with the present invention include sodium chloride, potassium chloride, sodium bromide and potassium bromide. The alkali metal halides preferably comprise from about 0.1% to about 10% by weight of the extinguishing composition.

In accordance with one embodiment of the present invention, there is provided a method for extinguishing fires which includes the use of a composition comprised of a hydrofluorocarbon and an acid-scavenging additive as a fire

extinguishing agent. The compositions may be applied in the variety of methods employed for other halogenated hydrocarbons, including application in a flooding system, portable system or specialized system. The extinguishant is effective in low concentrations, and of course, at high concentrations as well. The concentration employed may depend to some extent on the nature of the fire, the combusting material and the circumstances of application. Generally, application rates preferably range from about 1% to about 25% v/v, and more preferably from about 2% and to about 15% v/v, of the hydrofluorocarbon component in the atmosphere. The acid-scavenging additives comprise from about 0.1% to about 10% by weight of the composition.

The relative amounts of the hydrofluorocarbon and the acid-scavenging additive are not critical, but rather are dictated by the characteristics desired for the overall composition. For example, in certain applications there may be a greater need for low toxicity, and in other instances, the emphasis may be on cleanliness of the extinguishment.

The methods for application of the described fire extinguishing compositions are those known to be useful for the Halon agents. In broad terms, these methods utilize application systems which typically include a supply of agent, a means for releasing or propelling the agent from its container, and one or more discharge nozzles to apply the agent into the hazard or directly onto the burning object. Thus, the agents of this invention may be used in total flooding systems in which the agent is introduced into an enclosed region surrounding a fire at a concentration sufficient to extinguish the fire. In accordance with a total flooding system, equipment or even rooms may be provided with a source of agent and appropriate piping, valves and controls so as to automatically and/or manually be introduced at appropriate concentrations in the event that fire should break out. As is known to those skilled in the

art, the fire extinguishant may be pressurized with nitrogen or other inert gas at up to about 600 psig at ambient conditions.

Alternatively, the compositions of the invention may be applied to a fire through the use of conventional portable fire extinguishing equipment. It is usual to increase the pressure in portable fire extinguishers with nitrogen or other inert gases in order to ensure that the agent is completely expelled from the extinguisher. Systems in accordance with this invention may be conveniently pressurized at any desirable pressure up to about 600 psig at ambient conditions.

The invention will be further described with reference to the following specific Examples. However, it will be understood that these Examples are illustrative and not restrictive in nature.

EXAMPLE 1

A test facility with a total internal volume of 1440 cubic feet was constructed from 2x4 lumber and 3/4" plywood. The enclosure was equipped with two 3 foot by 3 foot windows and two standard doors located on opposite walls. The delivery system consisted of a standard Halon cylinder connected to 1" carbon steel pipe via a stainless steel flexhose, terminating in a standard Halon nozzle located 6 inches down from the center of the ceiling.

A large steel pan was filled with commercial n-heptane and placed in the center of the facility, and the n-heptane was then ignited. Thirty seconds after ignition, the doors to the enclosure were closed and the extinguishing agent released. The enclosure atmosphere was sampled after extinguishment of the fire by pulling a sample of the post-extinguishment atmosphere through a buffer solution contained in a polypropylene bubbler equipped with a 70 micron porous polyethylene frit. Fluoride and HF concentrations were determined employing a fluoride ion

selective electrode (ISE). The post-extinguishment atmosphere was sampled at two locations, one at a height of 6 feet and the second at a height of 2 feet, both sampling points located 2 feet diagonally out from the corner of the enclosure.

Sixty nine pounds of 1,1,1,2,3,3,3-heptafluoropropane (CF_3CHFCF_3) was discharged according to the above procedure and resulted in extinguishment of the fire. Analysis showed the concentration of HF to be 3535 ppm at the 6 foot location and 1948 ppm at the 2 foot location.

EXAMPLE 2

The procedure of Example 1 was repeated employing 69 pounds of 1,1,1,2,3,3,3-heptafluoropropane (CF_3CHFCF_3) to which had been added 1.0 pounds of dipentene (1.4 % by weight). Analysis showed the concentration of HF to be 2403 ppm at the 6 foot location and 1202 ppm at the 2 foot location.

This example demonstrates the advantageous effect of the addition of a small amount of an acid-scavenging additive to the hydrofluorocarbon. The amount of HF produced was reduced by 32% at the 6 foot location and by 38% at the 2 foot location.

EXAMPLE 3

The procedure of Example 1 was repeated employing a small steel pan filled with n-heptane. Analysis of the post-extinguishment atmosphere showed a concentration of HF of 50 ppm at the 6 foot location and 11 ppm at the 2 foot location.

EXAMPLE 4

The procedure of Example 3 was repeated employing 69 pounds of 1,1,1,2,3,3,3-heptafluoropropane (CF_3CHFCF_3) to which had been added 1.0 pounds of limonene (1.4 % by

weight). Following extinguishment of the fire, analysis showed the concentration of HF to be 32 ppm at the 6 foot location and 7 ppm at the 2 foot location.

This example demonstrates the advantageous effect of the addition of a small amount of an acid-scavenging additive to the hydrofluorocarbon. The amount of HF produced was reduced by 36% at both locations.

EXAMPLE 5

Testing of the fire suppressing and extinguishing capabilities of 1,1,1,2,3,3,3-heptafluoropropane with each of the following acid-scavengers yields similarly advantageous results: citral, citronellal, menthol, alpha-pinene, beta-pinene, camphor, vitamin A beta-carotene, isopoopenyl-1-1-methylcyclohexene, oleic acid, linoleic acid, palmitoleic acid, vaccenic acid, sodium chloride, potassium chloride, sodium bromide and potassium bromide. Desirable results are achieved for combinations of 90% to 99.9% by weight of the 1,1,1,2,3,3,3-heptafluoropropane and of 0.1% to 10.0% of the acid-scavenger. Similarly, suitable results are obtained for fire extinguishant compositions comprising blends of the foregoing acid-scavengers and the various other hydrofluorocarbons defined herein, including for example, trifluoromethane, pentafluoroethane, 1,1,1,2-tetrafluoroethane, 1,1,1,2,3,3-hexafluoropropane, 1,1,1,3,3,3-hexafluoropropane, 1,1,2,2,3,3-hexafluoropropane, 1,1,1,2,2,3,3-heptafluoropropane, 1,1,1,2,2,3,3,4,4-nonafluorobutane, 1,1,1,2,3,4,4,4-octafluorobutane and 1,1,1,3,3,3-hexafluorobutane. The foregoing compositions are effective in both total flooding and portable fire extinguishing systems, and work conventionally with typical, known propellants.

We claim:

1. A method for extinguishing a fire comprising the steps of:

a. introducing to the fire a fire extinguishing concentration of a composition comprising in combination:

(i) one or more hydrofluorocarbons of the formula $C_xH_yF_z$, wherein $(y+z) = (2x + 2)$, and wherein $y \leq x$; and

(ii) one or more substances selected from the group consisting of terpenes, unsaturated oils, sodium bicarbonate, potassium bicarbonate, monoammonium phosphate, alkali metal halides and urea; and

b. maintaining the concentration of the composition until the fire is extinguished.

2. The process of claim 1 wherein the composition is employed at a level of less than about 25% v/v of the hydrofluorocarbons.

3. The process of claim 1 wherein the extinguishing concentration of the compound is from about 1% to about 15% v/v of the hydrofluorocarbons.

4. The process of claim 1 wherein the composition is introduced by a total flooding system.

5. The process of claim 1 wherein the composition is introduced by a portable extinguishing system.

6. The process of claim 1 wherein the composition contains from about 90 to 99.9 percent by weight hydrofluorocarbon.

7. The process of claim 1 wherein the composition contains from about 0.1 to about 10 percent by weight of one or more

of the substances selected from the group consisting of terpenes, unsaturated oils, sodium bicarbonate, potassium bicarbonate, monoammonium phosphate, alkali metal halides and urea.

8. The process of claim 1 wherein the composition consists essentially of from about 90% to about 99.9% by weight of said hydrofluorocarbon and from about 0.1% to about 10.0% of said substance.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US95/03490

A. CLASSIFICATION OF SUBJECT MATTER
IPC(6) :A62D 1/08; A62C 13/00, 35/00
US CL :252/8, 2, 3; 169/46,47
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
U.S. : 252/8, 2, 3; 169/46,47

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
APS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US,A, 4,954,271 (Green) 04 September 1990, column 1 line 58 to column 2 line 47, and column 7 lines 27-53.	1-5, 7 -------- 6, 8
Y	US,A, 5,124,053 (Iikubo et al.) 23 June 1992, column 2 lines 11-36, and claims.	1-8
Y	US,A, 5,141,654 (Fernandez) 25 August 1992, column 2 line 55 to column 3 line 49.	1-8
Y	US,A, 5,084,190 (Fernandez) 28 January 1992, column 2 line 55 to column 3 line 39.	1-8
A	US,A, 3,879,297 (Languille et al.) 22 April 1975, column 2 lines 13 to column 3 lines 52.	1-8

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search
07 JUNE 1995

Date of mailing of the international search report
05 JUL 1995

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231
Facsimile No. (703) 305-3230

Authorized officer
Joseph D. Anthony
Telephone No. (703) 308-1235

INTERNATIONAL SEARCH REPORT

Int. ational application No.
PCT/US95/03490

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US,A, 4,826,610 (Thacker) 02 May 1989, abstract and column 2 lines 56-68.	1-8